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ORNL PROCESS WASTE TREATMENT PLANT MODIFICATIONS

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ABSTRACT

The ORNL Process Waste Treatment Plant removes low levels of radionuclides (primarily Cs-137 and Sr-90) from process waste water prior to discharge. The previous plant operation used a scavenging precipitation - ion exchange process which produced a radioactive sludge. In order to eliminate the environmental problems associated with sludge disposal, the plant is being converted to a new ion exchange process without the precipitation process.

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Introduction

The Process Waste Treatment Plant at Oak Ridge National Laboratory treats low-level aqueous waste collected from various locations at the laboratory. The current treatment plant was designed to use a scavenging-precipitation-ion exchange process and has been in operation since 1976. Prior to that a lime-soda-clay precipitation process was used. The scavenging-precipitation-ion exchange process has consistently produced an effluent well within the maximum permissible concentration limits for discharge to a public stream. The major disadvantage of the process is production of radioactively contaminated sludge. Disposal of the sludge in an environmentally acceptable manner is difficult and costly. For this reason alternate processes were investigated to eliminate the sludge production problem. The objective of this effort was to develop a process producing an acceptable effluent with reasonable capital and operating costs and no sludge generation.

Description of the Process Waste Treatment Plant¹

Figure 1 is a simplified process flow diagram of the existing treatment plant. The total treatment plant consists of: (1) the equalization basin; (2) the feed system, Building 3518; (3) process equipment, Building 3544; (4) the sludge disposal basin; and (5) radioactive-waste transfer piping. The first three components are located in the main ORNL area, the sludge disposal basin is located at Burial Ground No. 5 about 1.0 km south of the processing plant, and the waste transfer piping connects the processing plant with the disposal basin and the ORNL Intermediate-Level Waste System.

The equalization basin has existed for a number of years and has a capacity of 3.8×10^6 liters of low-level waste ($<1.0 \mu\text{Ci/liter}$), which is essentially ^{90}Sr and ^{137}Cs . Smaller quantities of ^{60}Co and ^{154}Eu are sometimes present.

Feed is pumped continuously from the basin through pipes, pumps, and valves located in Building 3518. Only minor modifications were made to this equipment to convert it from the previously used lime-soda process. Feed is pumped at a selected rate, usually between 175 and 375 liters/min, into the processing plant in Building 3544.

This building is divided into a control room, a chemical makeup area, and a shielded area containing regeneration-solution tanks, three ion exchange columns, an evaporator, a concentrated-waste tank, an acid off-gas scrubber, and pumps. The head-end treatment equipment, the sludge holdup and transfer system, and a concrete clearwell about 7 x 7 x 2 m are located on a concrete pad outside the building.

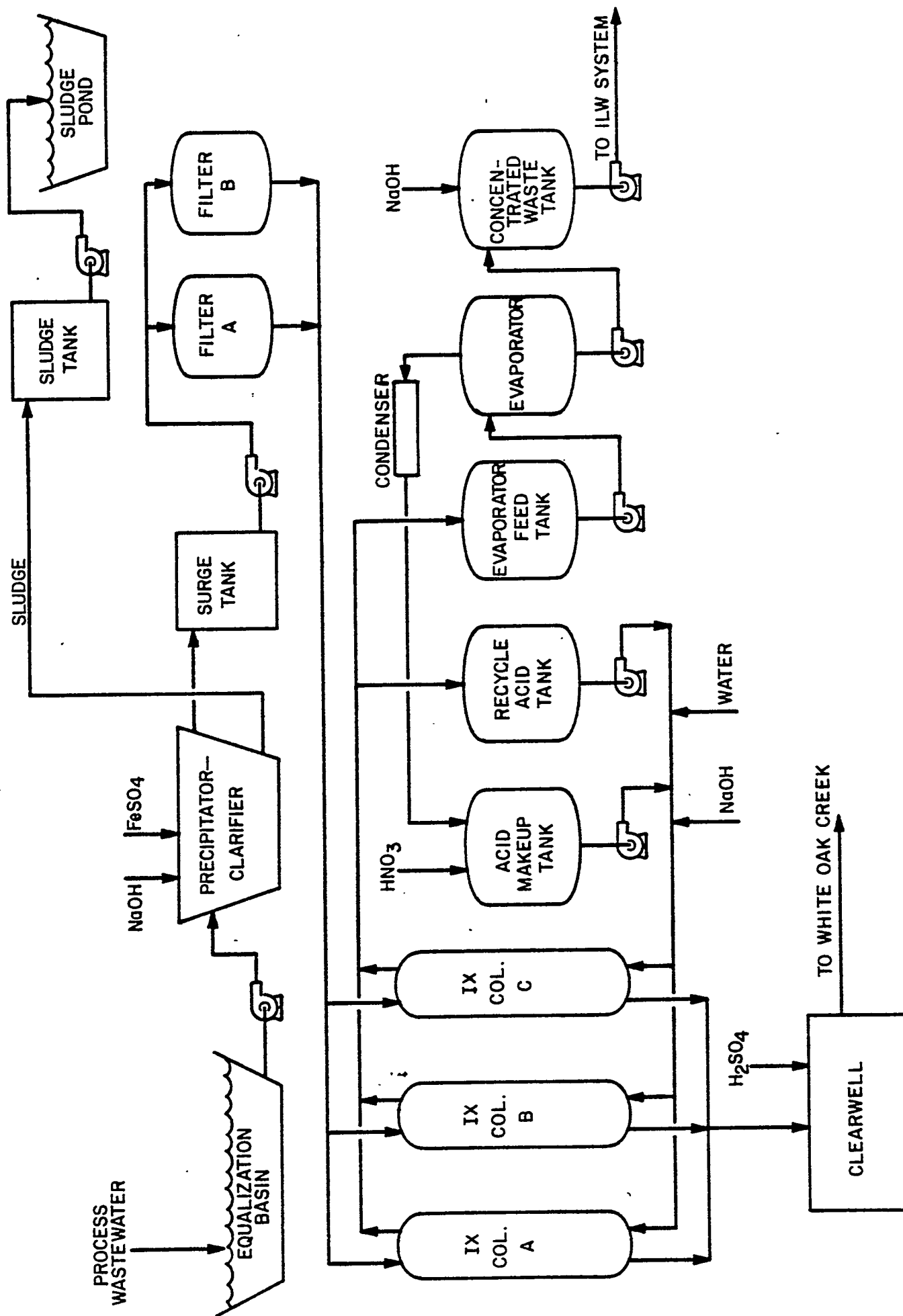


FIGURE 1
OLD PROCESS FLOW DIAGRAM

The sludge that is generated in the precipitator-clarifier is periodically pumped to the sludge disposal basin as a slurry containing 2 to 4 wt% solids.

The line connecting the process building to the sludge disposal basin is constructed of 2-in. schedule 80, unplasticized PVC pipe and is laid underground. The concentrated liquid waste from ion exchange regeneration, evaporation, and neutralization is pumped through an underground pipeline constructed of 1 1/2-in. schedule 40, type 304L stainless steel to the existing intermediate-level waste collection system.

Previous Operations of the Process Waste Treatment Plant¹

The treatment plant has been in continuous operation at an average flow rate of 300 liters/min. Occasionally, feed has been processed as fast as 565 liters/min. At no time has the plant effluent exceeded the maximum permissible concentration for water in public streams. The plant is designed for a maximum flow of 750 liters/min but has never operated at this rate.

The feed from the equalization basin is continually mixed with concentrated sodium hydroxide solution to give a pH of 11.8 and with a copperas (FeSO_4) solution to give 5 ppm iron. The hydroxide addition rate is controlled by an electrode downstream from the addition point in the feed. The ferrous solution rate is controlled by the setting on the feed pump. The feed then flows through a static pipe-mixer. Coagulation of the precipitate into larger particles occurs in the flocculator section of the precipitator-clarifier, where the mixture is gently agitated as it flows down to the bottom. The floc enters the bottom of the clarifier section, where separation is achieved by upflow of the mixture through a sludge blanket, which consists of fluidized particles that trap the floc and continue the precipitation reactions by crystal growth. These particles agglomerate and settle to form a slurry in the bottom of the vessel. This action scavenges radionuclides, dirt particles, and algae, as well as most of the hardness, from the waste stream.

The slurry is periodically pumped to an agitated 23,000-liter sludge holding tank and then to the sludge disposal basin, as necessary. This step removes from one-half to two-thirds of the total radioactivity in the stream. The proper operation of the clarifier section is monitored by turbidity analyses of samples taken at appropriate points in the stream.

The effluent from the clarifier overflows to a 25,000-liter surge tank and then is pumped through one of two pressure-type polishing filters containing a bed of 0.6 to 0.8-mm anthracite. When pressure drop increases 5 to 6 psi, the flow is switched to the other bed and the first one is backwashed. Backwashing is done at 2000 liters/min for 10 min with water from the clearwell. The bed is then re-

washed at 650 liters/min for 3 min, after which the wash solution is pumped back to the equalization basin.

From the filter, the stream, which now usually has less than 5 ppm hardness, passes downflow through one or more of three ion exchange columns containing 1275 liters of sodium-form Duolite CS-100 resin. The beds are used consecutively; a switch is made after the passage of about 2000 bed volumes of feed. The maximum flow rate through a bed is 380 liters/min, but two beds may be operated simultaneously, in parallel. A movable beta-gamma probe is mounted on the exterior of each column. In the pilot-plant development of the process, it was found that such a probe could be used to follow a band of maximum activity from top to bottom as the column was used and thus to predict breakthrough of radionuclides. Since the readings from these probes in plant operation have never been of value, their use has been discontinued.

To regenerate a resin bed, the column is eluted upflow with two batches (five bed volumes each) of 0.50 M nitric acid. The first batch removes most of the radioactivity and hardness and is then concentrated by evaporation, neutralized with sodium hydroxide, and sent to the Intermediate-Level Waste Treatment Plant. The second batch is stored and used as the first batch for the next elution. After a water rinse, the resin is reconverted to a sodium form by passing 20 bed volumes of 0.1 M NaOH upflow through the bed. The caustic and water washes are sent back to the equalization basin.

After leaving the ion exchange bed, the stream passes over a beta-gamma probe and into the first compartment of the clearwell. The readings from this monitor apparently cannot be correlated with any variable in the process and are therefore generally ignored.

The clearwell, which contains 80,000 liters, is divided into two sections by an overflow weir. Water in the first section, which holds two-thirds of the volume, backwashes the filters and makes up the 0.1 M NaOH for resin regeneration. At the weir, where a pH electrode continuously measures the pH, sulfuric acid is added to reduce the pH to 7.0. The waste then flows into White Oak Creek.

Description of Alternatives

Two process changes were considered. One concept would continue the precipitation-ion exchange process but substitute aluminum sulfate for ferrous sulfate as a flocculant. The sludge would be dissolved in nitric acid and discharged to the intermediate level waste ILW system. The second process eliminates the precipitation process and treats the waste after filtration with a strong acid cation exchange resin. In addition to the radionuclides, nonradioactive ions such as calcium, magnesium, and sodium would be removed by the resin. This would increase the resin loading and result in shorter run times and more frequent regeneration. The advantage of this process is that all of the radionuclides are dissolved in the

regenerant and are discharged to the ILW system. A separate sludge dissolution step is not required. Laboratory tests conducted by J. M. Chilton of the ORNL Chemical Technology Division confirmed the feasibility of the strong acid cation exchange process and established the process parameters. Since this process required fewer plant modifications and would be operationally simpler it was selected for further evaluation.

Two different approaches for modifying the treatment plant were considered. The first method involved using the three existing fixed-bed ion exchange columns refitted with strong acid cation exchange resin. A fourth column would be added to provide more capacity since the new process would have shorter service cycles.

Figure 2 is a process flow diagram of this system. For convenience wastewater will still flow through the precipitator/clarifier but no chemical additions will be made and no precipitation will occur. Wastewater is passed through the anthracite filters and then downflow through the ion exchange columns. Two columns in parallel will be run at the maximum flowrate of 750 ℓ /min. Since the resin is run in the hydrogen form the ion exchange effluent will be acidic. The effluent will be neutralized with NaOH in the clearwell prior to discharge to White Oak Creek.

Regeneration of the ion exchange resin is accomplished by passing 6 resin bed volumes of 3 N HNO_3 upflow through the columns followed by a water rinse. The first half of the acid regenerant is evaporated, neutralized and discharged to the ILW system. The second half is collected and reused as the first half of the next regeneration. The evaporator overhead is condensed and collected, brought up to 3N HNO_3 by strong acid addition, and used for the second half of the next regeneration. This regeneration process results in recovery of a large quantity of HNO_3 which would otherwise be wasted.

A second approach for modifying the process is to replace the existing fixed-bed columns with a single continuous, countercurrent ion exchange system. This would have the advantages of continuous operation and more efficient regeneration than the fixed-bed system. Operating cost savings would result from reductions in HNO_3 usage, NaOH needed for neutralization, steam for evaporation, and final disposal volume.

A process flow diagram for the continuous ion exchange system is shown in Figure 3. In the continuous countercurrent ion exchange system, the resin is moved around a single loop of connected vessels providing simultaneous treatment, regeneration, backwash and rinse cycles in separate sections without interrupting flow. The resin is moved in one direction, and the influent and all other solutions (regeneration, rinse, backwash) move in the opposite direction. The system operates by continuously cycling between a "run mode" and a "pulse mode". During the run mode of 5 to 20 minutes duration,

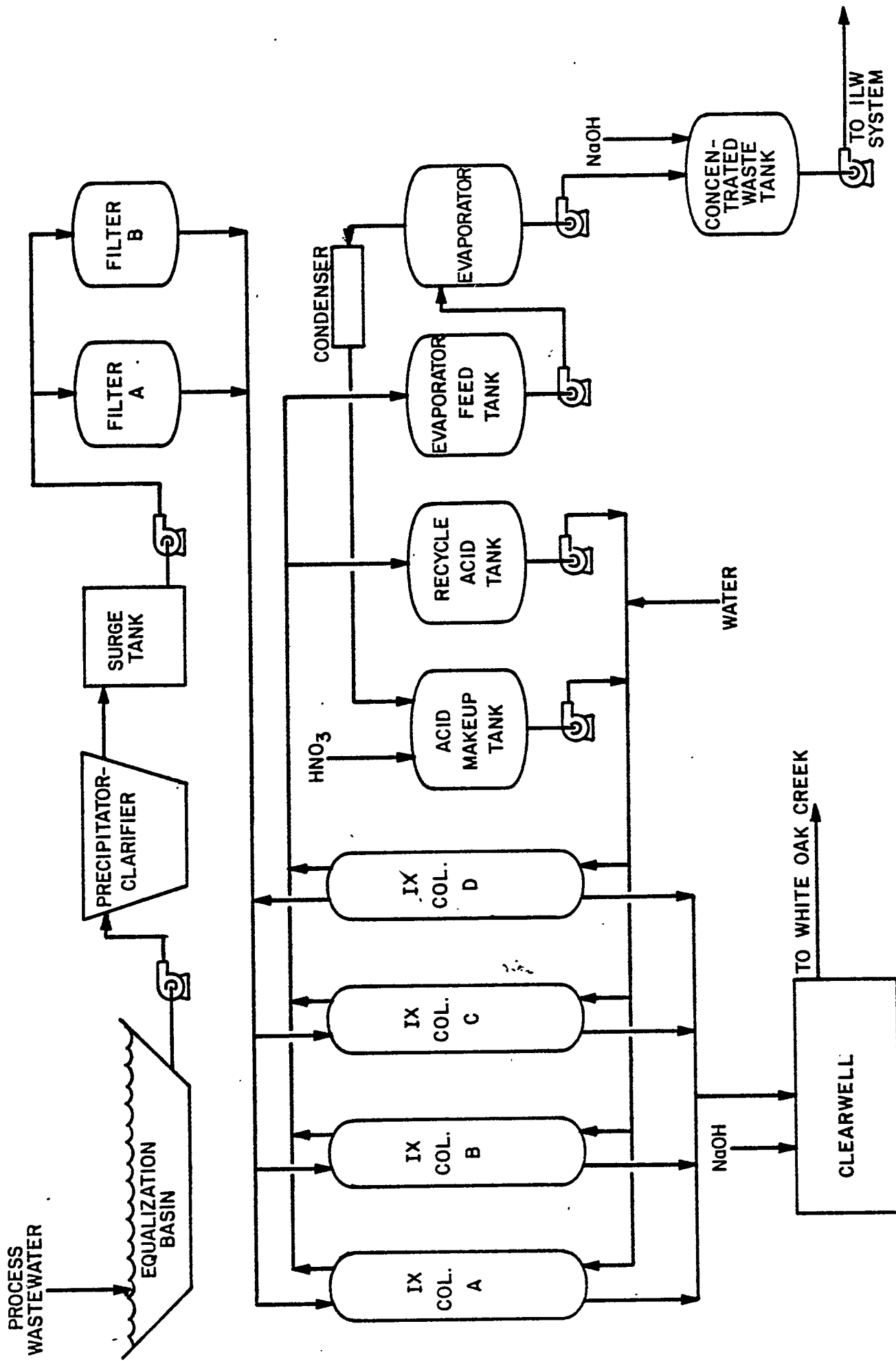


FIGURE 2
NEW PROCESS FLOW DIAGRAM

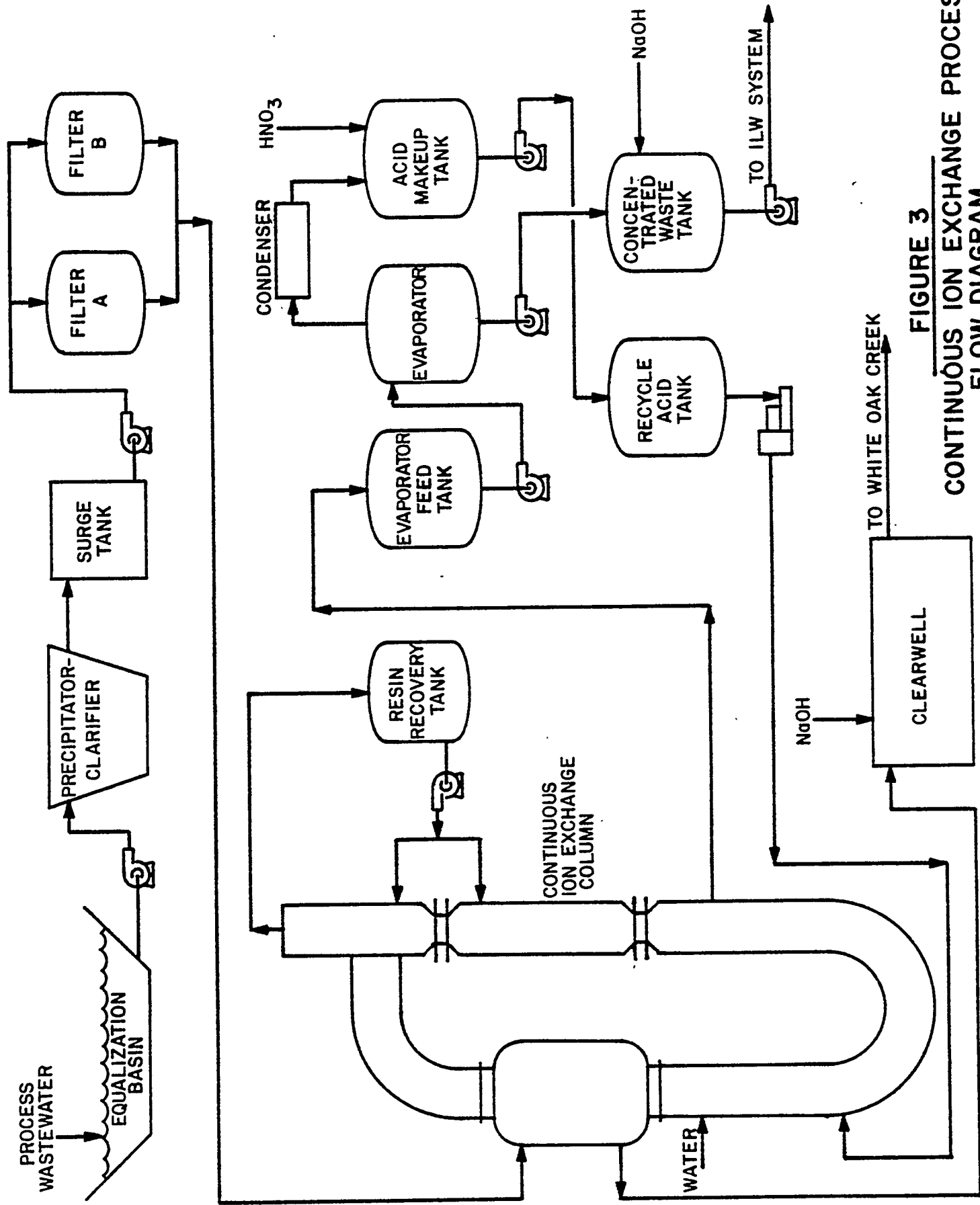


FIGURE 3
CONTINUOUS ION EXCHANGE PROCESS
FLOW DIAGRAM

three main valves of the contacting section and the regenerating section are closed. In the contacting section the waste feed stream is fed down through the resin bed and treated product water having a pH of 3 is delivered from the bottom of the bed.

Simultaneously, approximately 4N HNO_3 regenerant is fed through loaded resin in the regenerating section at the bottom of the loop and exits as nitrate salts after stripping the resin free of the sorbed ions. Spent regenerant solution flows to the evaporator feed tank and to the evaporator. At the same time, loaded resin is dropping through an open valve into the pulse section. Positive pulse control sensors close this valve when the pulsing section is properly filled.

Clear rinse water washes regenerant traces from the stripped resin (next to enter the contacting section). The valve for the water rinse is operated by a conductivity controller that senses the interface of rinse and regenerant solutions to insure all regenerant traces are removed before rinsing is terminated. In the "pulse mode", during which process waste, regenerant, and rinse flows are halted for 15 to 30 seconds, main valves of the contacting section and the regenerating section open to allow the compacted resin bed to be pushed counter-current to the direction of flow. A hydraulic pulse of raw water transfers resin around the loop by a pre-selected distance. This movement puts loaded resin from the pulse section into position for regeneration while pushing stripped and rinsed resin into the contacting section and moving loaded resin from the contacting section around to the resin storage area. A water backwash cleans resin fines and foreign particles from the loaded resin which is fluidized at this point. Resin fines and the exit water rinse are pumped to the resin recovery tank.

After ion exchange, the process waste stream, now stripped of radioactivity and hardness, flows to the clearwell where it is neutralized by addition of Na OH solution. Spent regenerant solution is evaporated and the concentrate is neutralized and pumped to the ILW system. Overhead from the evaporator is condensed and collected for reuse to recover the HNO_3 .

Evaluation of Alternatives

Either of the two concepts would accomplish the project objective. Both options eliminate the production of sludge and will produce an effluent of acceptable quality for discharge. It is expected that operating labor requirements will be similar although maintenance costs may be slightly higher for the continuous column.

The primary advantage of the continuous column over the fixed bed system is that it can be regenerated more efficiently, resulting in less regenerant waste. The increased regeneration efficiency results

in the use of less HNO_3 and NaOH , less steam for evaporation, and lower final disposal costs.

In order to determine the operating costs of the continuous counter-current ion exchange system and the four column fixed bed ion exchange column system, a series of calculations were made to determine the quantity of chemicals and steam used and the amount of concentrated waste created by each system on a daily basis. After computing the daily quantity of chemicals, steam, and waste used or formed, an annual operating cost was calculated for each system.

In making the calculations the following assumptions or data were used:

- a. The evaporator uses steam at 35 psig, which costs \$4.00 per 1000 pounds.
- b. All calculations are based on both systems having a design feed rate of 200 gpm.
- c. Chemical costs came from the July 13, 1981, edition of the Chemical Market Reporter while steam and final disposal costs were provided by L. C. Lasher of the ORNL Operations Division.
- d. Table 1 contains the data used in making the calculations.
- e. Only process chemical costs, steam costs, and final disposal costs are considered to be significant for the purpose of this study. All other costs remain approximately equal for both systems.
- f. Assumption was made that if the evaporator at the waste treatment plant was used and the regeneration waste was concentrated to a 7.0-7.4 N NO_3 salt concentration, then significant further concentration of this waste would not occur in the ILW system.

Table 2 is a comparison of the costs of operating each system and shows that the continuous column can be operated for approximately \$127,000 less per year than the fixed bed system.

Table 1. Data elements used in cost calculations

Item	Cost	Quantity used per day	
		Fixed bed column	Continuous column
60% HNO_3	\$8.75/100 lb	173 GPD	58.5 GPD
50% NaOH	\$300/ton	78.3 GPD	41.4 GPD
Steam @50 psig	\$4/1000 lbs	12216 lbs/day	2042.67 lbs/day
Final Waste Disposal	\$0.70/gal	304.3 GPD	121.5 GPD

Table 2. Comparison of costs

<u>Cost unit</u>	<u>Fixed bed column</u>			<u>Continuous column</u>		
	<u>Day</u>	<u>Month</u>	<u>Year</u>	<u>Day</u>	<u>Month</u>	<u>Year</u>
Nitric Acid (60%)	\$171.80	\$5145.00	\$61848.00	\$ 58.08	\$1742.70	\$20912.40
Caustic (50% NaOH)	149.50	4485.00	53820.00	79.05	2371.50	28458.00
Steam @ 50 psia	48.85	1465.80	17589.60	8.17	245.10	2941.20
Hydrofracture	213.00	6390.00	76680.00	85.05	2551.50	30618.00
Totals	\$583.15	\$17494.80	\$209937.60	\$230.35	\$6910.80	\$82929.60

Cost difference: \$352.80/day, \$10,584.00/month, or \$127,008.00/year in favor of continuous column.

Capital costs were estimated for both process modifications. Addition of the fourth fixed bed column was estimated to cost \$260,000. Addition of the continuous ion exchange column was estimated to cost \$860,000 or \$600,000 more than the fixed bed system.

Since the capital cost for the continuous column is greater than that for the addition of the fixed bed column, an economic analysis was made to determine whether additional capital could be justified by the operating cost savings.

The rate of return on the additional capital investment for the continuous column was computed using the discounted cash flow method. The initial capital outlay was taken as the difference between the costs of the continuous column system and the fixed bed system. The operating cost savings were taken as annual cash incomes. The operating cost savings were inflated at a rate of 10% per year. The life of the facility was assumed to be 10 years. The following is a summary of the economic data for this analysis:

Initial investment	\$600,000
Annual operating cost savings (first year)	\$127,000
Inflation rate for savings	10% per year
Life of facility	10 years
Salvage value of facility	0
Rate of return	25%

The 25% rate of return on the additional investment for the continuous column is marginally attractive. This investment, however, was considered in terms of the availability of capital and the competing uses of the available money. Since money for capital projects is limited, the lower cost option of adding the fourth fixed bed column was selected.

System Performance

Two of the existing ion exchange columns were filled with strong acid cation exchange resin to test the performance of the new process. Table 3 gives the results of the performance tests. The new process produces an effluent well within the discharge requirements. The length of a service cycle on each column was 600-700 resin bed volumes, confirming laboratory test data. This compares to approximately 2000 resin bed volumes with the old process.

Before the full scale test it was assumed that breakthrough of Cs ion would closely follow Na ion breakthrough. In fact, a sodium ion detector was proposed to determine the end of a cycle. In practice it was found that Cs was removed for a significant period after Na breakthrough had occurred indicating a high selectivity of the resin for Cs over Na.

Table 3 - Test Data
Average Concentrations Bg/l

	<u>Cs-137</u>	<u>Sr-90</u>
Influent	69	660
Effluent	4.3	1.3

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